

## Ultrathin Films of Amphiphilic Ionic Polyacetylenes

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**ABSTRACT:** Thin films of amphiphilic ionic polyacetylenes based on poly(*N*-octadecyl-2-ethynylpyridinium bromide) were formed using the Langmuir–Blodgett and layer-by-layer deposition techniques. The surface pressure–molecular area isotherms of the monolayers of these polymers at the air–water interface indicate that the alkyl (octadecyl) chains of the repeating units are oriented perpendicularly to the water surface while the rigid conjugated polymer backbones are located within the planar layer of the interface. The molecular organization of transferred polymer multilayers has been also studied by FT-IR, ATR, GAR, and ellipsometry. As a result of this study, a model of the molecular organization of ultrathin films is proposed, in which the conjugated backbone chains of the polymer molecules are oriented parallel to the substrate and are sandwiched between layers of interdigitated octadecyl groups. The electrical conductivity of the polymer films was found to increase substantially upon doping with iodine. Enhanced gas permeability and permselectivity of membranes from Nafion were achieved by deposition of ultrathin films of the above polyacetylene on these membranes.

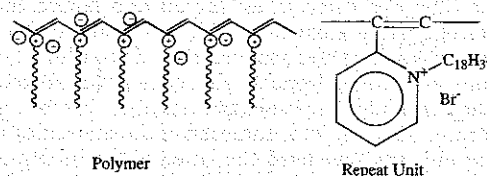
## Introduction

Polyacetylenes have been the focus of research in the field of molecular electronics as conducting wires. A large number of polyconjugated systems such as polyacetylenes and poly(diacetylene)s were also recently studied in the form of thin films.<sup>1</sup> We have recently reported on the synthesis and characterization of conjugated ionic poly(*N*-alkylethynylpyridinium bromides) with a long alkyl chain (C<sub>18</sub>H<sub>37</sub>) attached to the quaternized nitrogen. These polymers combine conjugation and amphiphilicity and are therefore prime candidates for the formation of two-dimensional conjugated systems.<sup>2</sup> The structure of these polymers is given in Figure 1. They were prepared by activation of the acetylenic bond through quaternization of the pyridine nitrogen, which resulted in a spontaneous polymerization of the triple bond.<sup>3–4</sup>

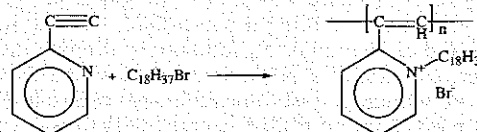
Control of the organization of a film on the molecular level is a very desirable feature for electronic applications. Techniques such as Langmuir–Blodgett film deposition and “layer-by-layer” self-assembly of polycation and polyanion are of interest. With both these approaches, thin films of ionic polyacetylenes with direct control over the degree and type of ordering and film thickness may be obtained. In this paper we report on the formation and characterization of thin films of a conjugated ionic polymer, poly(*N*-octadecyl-2-ethynylpyridinium bromide) [P2EPY/C<sub>18</sub>H<sub>37</sub>Br]. The uniform and facile formation of multilayers leads to layered systems which have potential in electro-optical, permeation, and permselectivity applications.

## Experimental Section

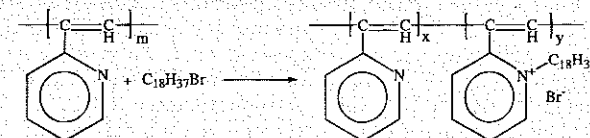
**1. Synthesis.** P2EPY/C<sub>18</sub>H<sub>37</sub>Br was prepared using two different synthetic approaches. The first approach involved the direct reaction of 2-ethynylpyridine (2-EPY) with 1-bro-



**Figure 1.** Schematic structure of P2EPY/C<sub>18</sub>H<sub>37</sub>Br.

a). P2EPY-C<sub>18</sub>H<sub>37</sub>Br Homopolymer

## b). P2EPY-q-octa Copolymer



**Figure 2.** Reaction schemes of the homopolymer and copolymer formation.

mooctadecane (1-BO). The second involved quaternization by 1-BO of uncharged poly(2-ethynylpyridine) (P2EPY) previously prepared by thermal polymerization.<sup>5</sup> A completely quaternized P2EPY/C<sub>18</sub>H<sub>37</sub>Br homopolymer was produced in the former reaction, while a random copolymer of 2-EPY and *N*-octadecyl-2-ethynylpyridinium bromide (P2EPY-q-octa) was obtained in the latter due to partial quaternization (25–30 mol %) of P2EPY. We should note that assignment of complete quaternization is based on the absence of the peak at –74 ppm corresponding to the unquaternized nitrogen in the <sup>14</sup>N-NMR spectrum, and the presence of residual unquaternized sites, at the level of sensitivity of NMR, may not be ruled out (see below). The details of synthesis and characterization of these polymers have been reported elsewhere.<sup>2</sup> The reaction schemes are shown in Figure 2.

**2. General Procedures and Characterization. Compression Isotherms and L–B Multilayers.** All pressure–area isotherm measurements and deposition of mono- and multilayers were carried out using a Lauda Langmuir Film-

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